REACTIONS OF ISOTOPICALLY LABELED NITRIC OXIDE (N^{15}O) IN A GAS PHASE CORONA REACTOR[#]

By

B.R. Locke, R.J. Clark+, G. Sathiamoorthy, and W.C. Finney
Department of Chemical Engineering
FAMU-FSU College of Engineering
Tallahassee, Florida 32310-6046
+Department of Chemistry
Florida State University
Tallahassee, Florida 32306-3006

ABSTRACT

The chemical reactions of nitric oxide decomposition in a pulsed streamer corona discharge were studied through the use of isotopically labeled nitric oxide, N^{15}O. Detection of the relative abundance of N^{14}-N^{14}, N^{15}-N^{14}, N^{15}-N^{15} and N^{15}O using mass spectrometry indicate that decreasing the initial concentration of NO leads to less direct dissociation of N^{15}O by the corona discharge in favor of direct dissociation of N^{14}-N^{14}. It was found that even at a concentration of 5% NO in a nitrogen carrier gas, the ratio of N$_2$ formed from N^{15} reacting with N^{15} to that formed from N^{15} reacting with N^{14} was 0.3. These results are consistent with expectations from previous studies in the literature, however, the present study offers the potential for direct measurement of reaction pathways in the corona reactor to assess more accurately the magnitude of reaction rate constants and the relative importance of various reaction pathways.

INTRODUCTION

A large number of experimental studies have been conducted to study the decomposition of nitrogen oxides in gas phase pulsed corona reactors as functions of the gas composition, the discharge and electrical field conditions, and other parameters including reactor residence time [1,2,4-7]. Similarly, a number of theoretical studies have been conducted to develop mathematical models of pulsed corona discharge characteristics and reaction kinetics [3, 8]. Comparison of mathematical models with experimental data has shown that the general trends predicted by the models are reflected in the experimental data [8], however, detailed quantitative comparisons of model output
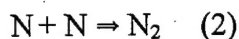

[#] International Symposium on Non-Thermal Discharge Plasma Technology for Air Pollution Control, Beppu and Oita, Japan, December 22-23, 1997.

with experimental data has been difficult due to the large number of reaction rate parameters needed in the models as well as to the complex physical and chemical [1]phenomena occurring in the non-thermal plasma. The present study focuses on a single aspect of this problem, namely, the use of isotopically labeled nitric oxide ($N^{15}O$) in an atmosphere of nitrogen. Analysis was made by mass spectrometry to quantify the importance of various reaction pathways.
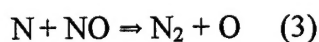
In a gas consisting primarily of molecular nitrogen (N_2) and nitric oxide (NO) the pulsed corona is known to lead to nitrogen dissociation through:
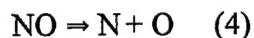
$$N_2 \Rightarrow 2N \quad (1)$$
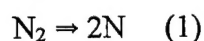
The dissociated nitrogen recombines with other nitrogen species:

$$N + N \Rightarrow N_2 \quad (2)$$

or by reaction with NO through

$$N + NO \Rightarrow N_2 + O \quad (3)$$

It has normally been assumed that the direct reaction of NO with electrons produced in the pulsed corona is negligible when the concentration of NO is low, i.e., the following reaction is small:

$$NO \Rightarrow N + O \quad (4)$$

It is generally difficult to measure the amount of nitrogen recombination in the above reactions since the additional molecular nitrogen formed by recombination is always likely to be small in comparison to the molecular nitrogen present in the carrier. In order to overcome this obstacle, the present study uses the labeled nitrogen isotope N^{15}

---

[1] International Symposium on Non-Thermal Discharge Plasma Technology for Air Pollution Control, Beppu and Oita, Japan, December 22-23, 1997.

in the feed NO. Analysis by mass spectrometry will distinguish and quantify the above reactions through measurement of the magnitudes of the peak associated with the mass 28, 29, 30, and 31.

EXPERIMENTAL APPARATUS AND METHODS

The pulsed corona reactor used in this study was a 2.5 cm inside diameter, 15 cm long, stainless steel, cylindrical tube. The stainless steel high voltage electrode was 1.5 mm in diameter with an effective active treatment length of 12.7 cm. This electrode was suspended concentric to the grounded outer cylinder giving an electrode spacing of 1.06 cm. The active pulsed corona treatment volume was 45.4 ml, and the reactor was operated in the batch mode.

Nitric oxide (NO) labeled with the non-radioactive isotope N^{15} was obtained from Cambridge Isotope Laboratories, Inc (Andover, MA), and high purity nitrogen gas (N^{14}-N^{14}) was obtained from Air Products (Allentown, PA). The reactor was filled with either 5% $N^{15}O$ in N_2 or 10% $N^{15}O$ in N_2 and a set of three runs was conducted at the three reactor residence times of 4, 6, and 12 minutes for each feed condition. The applied pulsed voltage was maintained constant at 18 kV for all runs. After each run, the reactor was sampled and the gases were analyzed on a Hewlett Packard GC/MS system. The mass peaks at 28, 29, 30, and 31 molecular weight were monitored. After each sample was analyzed, a small amount of oxygen and water were added to the reactor and the samples were reanalyzed on the GC/MS to remove the $N^{14}O$ and $N^{15}O$ from the observed 30 and 31 mass peaks.

The power supply was similar to the configuration used by Clements et al. (1989) [1]. A high voltage DC T-R set was modified by eliminating the internal rectifier, thereby producing 0-100 kV AC at 0-28 mA. Output from the T-R set was connected to the pulse generation circuit, where the current passes through a high voltage resistor (333 $\kappa\Omega$) and then through a diode array which acts as a half-wave rectifier. The output from the rectifier charges a bank of capacitors (2700 pF) during the charging cycle. A mechanical rotating spark gap having two fixed stainless steel spherical electrodes and a rotating rod electrode was employed to discharge the capacitor bank twice per shaft revolution, synchronized with the AC input current (60 Hz). From the output of the spark

gap the circuit had two parallel pathways. One pathway passes through a load resistor (145 kΩ) which enables the gap to fire. The other was connected to the central wire within the cylindrical reactor, from which the discharge emanated.

RESULTS

Measurement of the relative abundance of N^{15}- N^{14} and N^{15}- N^{15} as well as the concentration of $N^{15}O$ by GC-MS for reactor exposure times of 4, 6, and 12 minutes showed that as the exposure time increased the amount of NO decreased as expected. Table 1 summaries the experimental data for these runs. The 31 mass peak ($N^{15}O$) decreases monotonically with residence time for both sets of runs at the 5% and 10% initial NO concentration. The mass 28 peaks (N^{14}-N^{14}), also as expected, do not change during the course of the runs. The mass 29 and 30 peaks can be shown to consist primarily of N^{15}-N^{14} and N^{15}-N^{15} by introducing a small amount of oxygen and water to react with the NO in each sample. The data indicated by the "after washing" label in Table 1 is for the same samples and runs as shown above that label, but after the addition of water and oxygen. This data shows very little change in the relative abundance of the 29 and 30 peaks and complete elimination of the 31 peak, indicating that most of the value of the 31 peak is from $N^{15}O$ and that the 30 mass peak is predominantly N^{15}-N^{15}. The results for the 5% and 10% NO feed are comparable in this respect.

For the higher initial NO concentration (10%) the ratio of N^{15}- N^{15} to N^{15}- N^{14} was approximately 0.54 to 0.57 and did not significantly change with reactor residence time. At the lower initial NO concentration, however, the ratio was 0.30 at the 6 minute residence time and 0.38 at the 12 minute residence time. This indicates that at the higher initial NO concentration, more N^{15} from the dissociation of the NO is available for recombination to form molecular nitrogen. As the concentration of NO decreases the probability of combination of N^{15} with the N^{14} from the nitrogen dissociation increases. It is significant, and surprising, that even at 10% and 5% total NO the probability of reaction of N^{15} with N^{15} is fairly large in comparison with the reaction of N^{15} with N^{14}. This is consistent with the hypothesis that treatment in the pulsed corona reactor more readily leads to NO dissociation than to N_2 dissociation.

CONCLUSIONS

The present study provides preliminary data on the use of isotopically labeled nitric oxide to study reaction pathways in a pulsed streamer corona discharge. The general results indicate that in nitrogen gas with 5% and 10% concentrations of nitric oxide, the direct dissociation of NO by the pulsed corona discharge is highly significant, however, as expected, the relative importance of this reaction decreases as the concentration of NO decreases. Further studies in different atmospheres, including the addition of oxygen and water vapor to the reactor, and more extensive variation of reactor residence time and field conditions coupled with the use of kinetic models can be used to quantify the reaction rate coefficients and the reaction pathways.

ACKNOWLEGMENTS

REFERENCES

1) Clements, J.S., A. Mizuno, W.C. Finney, and R.H. Davis, "Combined Removal of SO_2, NOx, and Fly Ash from Simulated Flue Gas Using Pulsed Streamer Corona", *IEEE Trans. On Ind. Appl.*, **25**, No.1, January/February 1989, 62-69.

2) Gallimberti, I., "Impulse Corona Simulation for Flue Gas Treatment", *Pure Appl. Chem.*, **60** (1988) 663.

3) Lowke, J.J., and R. Morrow, "Theoretical Analysis of Removal of Oxides of Sulfur and Nitrogen in Pulsed Operation of Electrostatic Precipitators", *IEEE Transactions on Plasma Science*, **23**, (1995) 661-678.

4) Masuda, S., and Y. Wu, "Removal of NO_x by Corona Discharge Induced by Sharp Rising Nanosecond Pulsed Voltage", *Inst. Phys. Conf. Ser. (Electrostatics '87)*, IOP Pub. Ltd., U.K., 249-254.

5) Masuda, S., and H. Nakao, "Control of NO_x by Positive and Negative Pulsed Corona Discharges", *IEEE-IAS Trans.*, **26** (1990) 374-383.

6) Mizuno A., J.S. Clements, and R.H. Davis, "A Method for the Removal of Sulfur Dioxide from Exhaust Gas Utilizing Pulsed Streamers for Electron Energization", *IEEE Transactions on Industry Applications*, **IAS-22**, 1989, 516-522.

7) Ohkubo, T., S. Kanazawa, Y. Nomoto, J. S. Chang, and T. Adachi, "NO_x Removal by a Pipe with Nozzle-Plate Electrode Corona Discharge System", *IEEE Trans. Ind. Appl.*, **30** (1994), 856-860.

8) Penetrante, B.M., M.C. Hsiao, B.T. Merritt, G.E. Vogtlin, and P.H. Wallman, "Comparison of Electrical Discharge Techniques for Nonthermal Plasma Processing of NO in N_2", IEEE Transactions on Plasma Science, **IAS-23** (1995), 679-687.

Table 1. – N^{15}O Experimental Results

10% NO Feed in N$_2$	4 minutes	6 minutes	12 minutes
Mass Spec Mole Wt.	Relative GC/MS mass reading	Relative GC/MS mass reading	Relative GC/MS mass reading
28	1000	1000	1000
29	10.5	12.3	18.2
30	6.0	6.5	9.8
31	37.5	28.6	13.0
30/29	0.58	0.53	0.54
After washing			
28	1000	1000	1000
29	11.1	11.9	19.1
30	5.3	5.4	9.1
31	0	0	0
30/29	0.48	0.46	0.48
5% NO in N2			
28		1000	1000
29		12.2	16.2
30		3.7	6.1
31		6.4	2.4
30/29		0.30	0.38
After washing			
28		1000	1000
29		10.3	14.8
30		2.9	5.2
31		0	0
30/29		0.29	0.35